

Supporting Information

Binuclear Organometallic Ruthenium Complexes of a Schiff Base Expanded Porphyrin

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Supplementary Figures

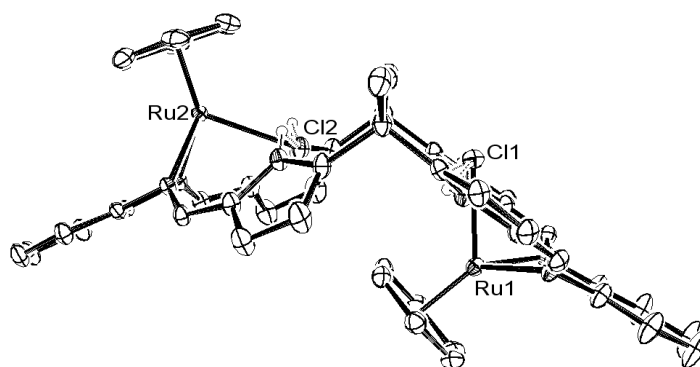


Figure S1. Side view of the cation of compound **2** showing a partial atom-labeling scheme. Displacement ellipsoids are scaled to the 30% probability level. Most hydrogen atoms have been removed for clarity. The dashes lines are indicative of H-bonding interactions

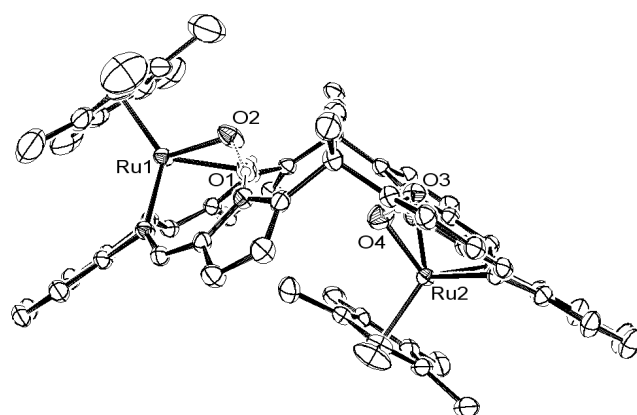


Figure S2. Side view of the cation of compound **3** showing a partial atom-labeling scheme. Displacement ellipsoids are scaled to the 30% probability level. Most hydrogen atoms have been removed for clarity. The dashed lines are indicative of H-bonding interactions

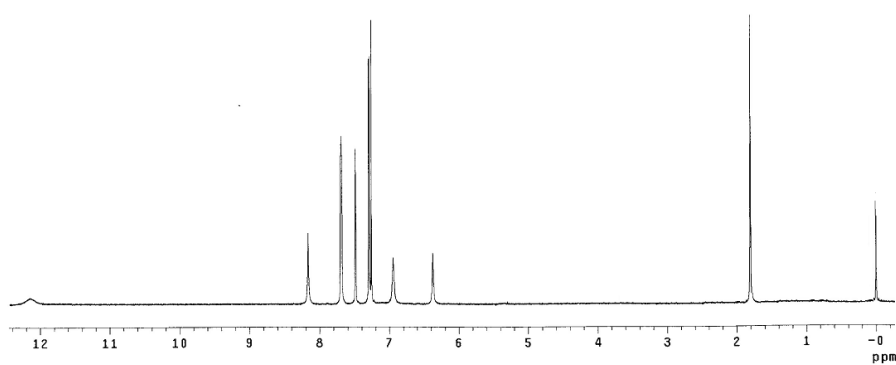


Figure S3. ^1H NMR spectrum of complex **2** at room temperature in CDCl_3 .

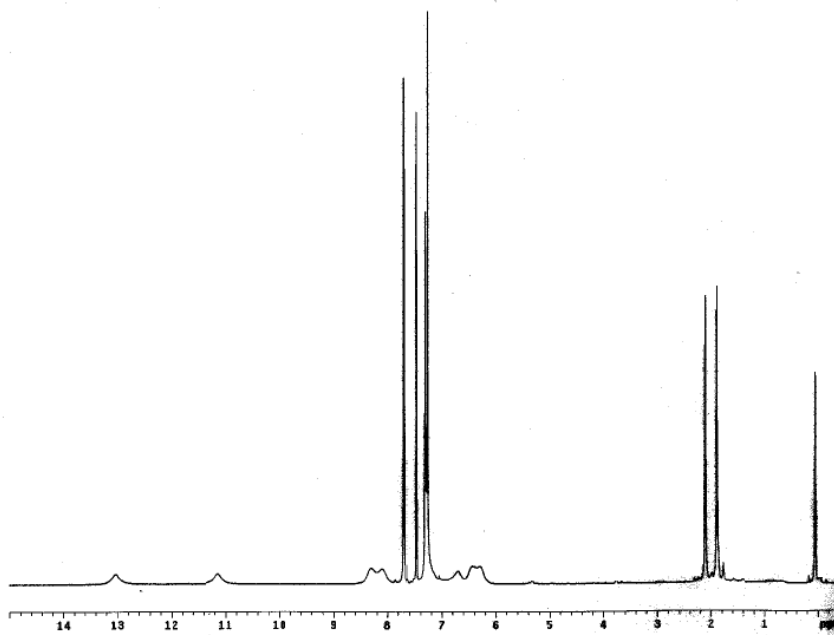


Figure S4. NMR spectrum of complex **2** at -50 °C in CDCl₃.

General Experimental Procedures

Prior to use, all glassware was soaked in KOH-saturated isopropyl alcohol for ca. 12 h and then rinsed with water and acetone before being thoroughly dried. Dichloromethane was freshly distilled from CaH₂. *n*-Pentane was stirred over concentrated H₂SO₄ for more than 24 h, neutralized with K₂CO₃, and distilled from CaH₂. Diethyl ether was dried by passage through two columns of activated alumina. Deuterated solvents were purchased from Cambridge Isotope Labs and used as received. [$\{\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{Cl})\}_2(\mu\text{-Cl})_2$] was purchased commercially (Strem) and used as received, $[\text{Ru}(\text{Cp}^*)(\text{CH}_3\text{CN})_3][\text{PF}_6]$ and NaBAR₄ (Ar' = 3,5-bis(trifluoromethyl)phenyl) were prepared following reported procedures.^{1,2} Solutions were stirred magnetically.

Nuclear magnetic resonance (NMR) spectra were obtained on a Varian Mercury 400 MHz. High-resolution mass spectra were obtained at the University of Texas at Austin, Department of Chemistry and Biochemistry, Mass Spectrometry Facility. Elemental

analyses were performed by Midwest Microlabs Inc., Indianapolis, IN.

Synthetic details

Complex 2. [$\{\text{Ru}(\eta^6\text{-C}_6\text{H}_6)(\text{Cl})\}_2(\mu\text{-Cl})_2$] (40 mg, 0.08mmol) and NaBAr'_4 (142 mg, 0.16 mmol) were added to a suspension of the free base macrocycle **1** (50.0 mg, 0.08 mmol) in dry CH_2Cl_2 (30 mL) under an argon atmosphere. The mixture was stirred for 8 h affording a bright orange solution. The solvent was evaporated under reduced pressure. The air stable orange solid obtained in this way was purified by column chromatography (alumina, 1% $\text{MeOH}/\text{CH}_2\text{Cl}_2$). The first orange fraction was collected and the resulting product was crystallized from $\text{CH}_2\text{Cl}_2/n$ -pentane to yield 115 mg of complex **2** (51 %). ^1H NMR (100.6 MHz, 296 K, CD_3Cl): 12.20 (s, 4H, NH), 8.17 (s, 4H, CHN), 7.68 (s, 16H, H_o BAr'₄), 7.48 (s, 8H, H_p BAr'₄), 7.30-7.28 (m, 20H, ArH + Ph), 6.95 (m, 4H, pyrrolic CH), 6.38 (m, 4H, pyrrolic CH), 1.91 (s, 12H, CH_3). ^{13}C NMR (400 MHz, 296 K, Acetone-*d*₆): 161.7 (c, 50.1 Hz), 151.3, 148.0, 134.8, 133.7, 128.9 (c, 31.5 Hz), 124.5 (c, 272.7 Hz) 122.1, 117.5, 116.4, 116.1, 105.7, 35.6, 27.9. HR-ESI (m/z): 517.0728 (calc. For $\text{C}_{50}\text{H}_{48}\text{N}_8\text{Cl}_2\text{Ru}_2^{2+}$ 517.0737). Anal. Calcd. for $2\cdot(\text{CH}_2\text{Cl}_2)_2\text{C}_{119}\text{H}_{79}\text{B}_2\text{Cl}_6\text{F}_{48}\text{N}_8\text{Ru}_2$: C, 48.13; H, 2.68; N, 3.77. Found: C, 48.29; H, 2.37; N, 3.58. mp > 200 °C.

Complex 3. $[\text{Ru}(\text{Cp}^*)(\text{CH}_3\text{CN})_3][\text{PF}_6]$ (83 mg, 0.17mmol) was added to a suspension of the free base macrocycle **1** (50.0 mg, 0.08 mmol) in dry CH_2Cl_2 (30 mL) under an argon atmosphere. The reaction mixture is stirred for 10 min. The yellow slurry became a dark orange solution. At this point the reaction mixture is exposed to air, stirred for 20 min, and then concentrated to a volume of 5 mL. Addition of *n*-pentane (15 mL) caused the precipitation of a red-orange solid, which was washed with diethyl ether (2 x 10 ml) and dried under vacuum. Crystals grew as dark orange needles by slow diffusion of *n*-pentane into a CH_2Cl_2 solution of compound **3**. (99 mg, 81%). ^1H NMR (400 MHz, 296 K, acetone-*d*₆): 13.45 (s, 2H, NH), 13.22 (s, 2H, NH), 8.84 (s, 2H, CHN), 8.65 (s, 2H, CHN), 7.31-7.33 (m, 8H, ArH), 6.78 (m, 2H, pyrrolic CH), 6.73 (m, 2H, pyrrolic CH), 6.38 (m, 4H, pyrrolic CH), 2.27 (s, 3H, CH_3), 1.86 (s, 3H, CH_3), 1.57 (s, 3H, CH_3), 1.55 (s, 15H, Cp^{*}), 1.37 (s, 3H, CH_3), 0.92 (s, 15H, Cp^{*}). ^{13}C NMR (100.6 MHz, 296 K, acetone-*d*₆): 158.7, 158.1, 154.1, 153.3, 152.9, 150.7, 149.7, 128.9, 127.8, 119.1, 118.7, 112.0, 110.5, 107.3,

107.1, 106.8, 96.9, 96.1, 37.0, 36.9, 8.9, 8.6, 8.4, 8.2, 7.9, 2.4. HR-ESI (m/z): 538.6704 (calc. For $C_{58}H_{65}N_8Ru_2^{2+}$ ([M]-2O₂) 538.6698). Anal. Calcd. for $3 \cdot (CH_2Cl_2)_3$ $C_{61}H_{72}Cl_6F_{12}N_8O_4P_2Ru_2$: C, 43.45; H, 4.38; N, 6.65. Found: C, 43.18; H, 3.99; N, 6.51. mp > 200 °C.

X-ray experimental

The data were collected on a Nonius Kappa CCD diffractometer using a graphite monochromator with MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Data collections were conducted at 153 K using an Oxford Cryostream low temperature device.

Data reductions were performed using DENZO-SMN.³ The structures were solved by direct methods using SIR97⁴ and refined by full-matrix least-squares on F^2 with anisotropic displacement parameters for the non-H atoms using SHELXL-97.⁵

The following definitions apply to all the refinements:

$R = \Sigma(|F_0| - |F_c|) / \Sigma|F_0|$ for reflections with $F_0 > 4(\Sigma(F_0))$,

$R_w = \{\Sigma w(|F_0|^2 - |F_c|^2)^2 / \Sigma w|F_0|^4\}^{1/2}$, where w is the weight given each reflection,

Goodness of fit, $S = [\Sigma w(|F_0|^2 - |F_c|^2)^2 / (n - p)]^{1/2}$,

where n is the number of reflections and p is the number of refined parameters.

Unless otherwise specified, hydrogen atoms were calculated in ideal positions with isotropic displacement parameters set to $1.2 \times U_{eq}$ of the attached atom ($1.5 \times U_{eq}$ for methyl hydrogen atoms). Neutral atom scattering factors and values used to calculate the linear absorption coefficients are from the International Tables for X-ray Crystallography.⁶

Complex 2. Crystals grew as orange prisms by slow diffusion of *n*-pentane into dichloromethane. The data crystal was a prism that had approximate dimensions 0.25 x 0.25 x 0.20 mm. A number of the trifluoromethyl groups were disordered. The disorder model for each group was treated in the same way. The geometry of the trifluoromethyl groups was restrained to be equivalent throughout the refinement. The site occupancy factor for one component of one group was assigned the variable x , while the site occupancy factor for the second component of that same group was assigned to $(1-x)$. A common isotropic displacement parameter was refined for all fluorine atoms of the affected group while refining the variable x . When the value of x stabilized, the site occupancy factors for the two components were fixed at x and $1-x$ and the displacement parameters for

the fluorine atoms were refined independently of each other. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0486*P)^2 + (8.7617*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.142, with $R(F)$ equal to 0.0541 and a goodness of fit, S , of 1.40. The data were corrected for secondary extinction effects. The correction takes the form: $F_{corr} = kF_c/[1 + (1.1(2) \times 10^{-6}) * F_c^2 \lambda^3/(\sin 2\theta)]^{0.25}$, where k is the overall scale factor. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography (1992).⁶

Complex 3. Crystals grew as dark laths by slow diffusion of *n*-pentane into dichloromethane. The data crystal was cut from a larger crystal and had approximate dimensions 0.25 x 0.15 x 0.10 mm. A molecule of dichloromethane was severely disordered. Attempts to model the disorder were unsatisfactory. The contributions to the scattering factors due to this solvent molecule were removed by use of the utility SQUEEZE in PLATON98.⁷ PLATON98 was used as incorporated in WinGX.⁸ One of the hexafluorophosphate anions was disordered. The disorder appeared to involve the fluorine atoms while leaving the phosphorus atom fairly well behaved. A disorder model consisting of two orientations of octahedrally distributed fluorine atoms about a central phosphorus atom was constructed. The site occupancy factor for one set of fluorine atoms was assigned the variable x , while the site occupancy factor for the alternate orientation of fluorine atoms was assigned $(1-x)$. A common isotropic displacement parameter was refined for all the fluorine atoms in the anion. Geometric restraints were applied throughout the refinement so that the geometry of each orientation remained approximately octahedrally oriented around the phosphorus atom. In this way, the site occupancy for one component of the anion consisting of atoms F7, F8, F9, F10, F11 and F12 refined to 53%. Ultimately, the atoms of this anion were refined anisotropically with their displacement parameters restrained to be approximately isotropic. The function, $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, where $w = 1/[(\sigma(F_o))^2 + (0.0543*P)^2 + (3.3433*P)]$ and $P = (|F_o|^2 + 2|F_c|^2)/3$. $R_w(F^2)$ refined to 0.149, with $R(F)$ equal to 0.0621 and a goodness of fit, S , of 1.41. The data were checked for secondary extinction effects but no correction was necessary. Neutral atom scattering factors and values used to calculate the linear absorption coefficient are from the International Tables for X-ray Crystallography(1992).⁶

Table S1 Crystal data and structure refinement parameters for complexes **2** and **3**.

	2	3
empirical formula	C ₁₁₇ H ₇₅ B ₂ F ₄₈ N ₈ Ru ₂	C ₅₈ H ₇₂ F ₁₂ N ₈ O ₄ P ₂ Ru ₂
formula weight	2926.90	1686.05
crystal system	triclinic	triclinic
space group	P-1	P-1
<i>a</i> , Å	13.1378(10)	13.9012(5)
<i>b</i> , Å	15.2769(10)	15.6004(5)
<i>c</i> , Å	32.233(3)	18.3620(7)
α , °	97.5700(10)	65.919(1)
β , °	92.6880(10)	76.396(1)
γ , °	105.1710(10)	76.499(11)
<i>V</i> , Å ³	6167.0(8)	3490.8(2)
<i>Z</i>	2	2
<i>D</i> (Calc'd), mg/m ³	1.576	1.604
abs. coeff., mm ⁻¹	0.477	0.792
<i>F</i> (000)	2920	17086
crystal size, mm	0.25 × 0.25 × 0.20	0.25 × 0.15 × 0.10
θ for data collection, °	1.78 – 27.28	1.80 – 27.49
limiting indices	-16 ≤ <i>h</i> ≤ 16 -19 ≤ <i>k</i> ≤ 19 -32 ≤ <i>l</i> ≤ 41	-18 ≤ <i>h</i> ≤ 17 -19 ≤ <i>k</i> ≤ 20 -18 ≤ <i>l</i> ≤ 23
reflections collected	36580	23666
independent reflections	27059	15732
completeness to θ_{max}	97.6 %	98.2 %
absorption correction	none	none
data/restraints/parameters	27059 / 3018 / 1902	15732 / 315 / 897
goodness-of-fit on <i>F</i> ²	1.108	1.276
<i>R</i> , <i>R</i> _w	0.0541, 0.1286	0.0621, 0.1491

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